

FINAL REPORT

EMISSIONS FROM BIODIESEL BLENDS AND NEAT BIODIESEL
FROM A 1991 MODEL SERIES 60 ENGINE
OPERATING AT HIGH ALTITUDE

TO

NATIONAL RENEWABLE ENERGY LABORATORY

BY

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1.0 INTRODUCTION AND SUMMARY

The purpose of this study was to investigate the effect of adding methylsoyester, biodiesel, to a base diesel fuel on emissions from a Detroit Diesel Series 60 engine. The engine chosen is a modern four stroke engine with 1991 calibration. The hardware is typical of current on-road engine technology and has been extensively used for fuel emission studies (Unman, et al., 1990). Thus, the impact of various fuel compositions on emissions from the series 60 is well established. The 1991 Series 60 is also the engine specified by the California Air Resources Board for California diesel fuel certification.

In the current investigation, regulated emissions NO_x , CO, THC, and PM were determined for five fuels. These were a reference diesel, and candidate 200A, 35%Yo, 65% and 100% methyl soyester blends in the reference diesel.

The reference diesel, a low sulfur, 30% aromatic content, commercial Number 2 diesel fuel without additives, was obtained from Colorado Petroleum, Inc. Soyester was supplied by Interchem, Kansas City, MO, and manufactured by Procter and Gamble. Fuel analyses are reported in the body of the report. Testing was conducted following the EPA heavy duty transient test protocol. Composite testing was performed; for the reference and each candidate fuel, one cold test and up to three hot tests were conducted. Each candidate fuel was also bracketed by three hot tests on the reference diesel. In this way, the effect of engine drift on emissions could be separated from fuel effects.

All testing was performed against the reference diesel map. This does not conform with the Code of Federal Regulations which requires a separate map for each fuel for engine certification purposes. However, this has become the accepted way to examine the effect of fuel properties on emissions by EPA, industry groups like CRC, and state agencies like CARB

The results of the testing are in general agreement with studies on other engines. As the soyester composition increased, the NO_x emission increased, while the THC, CO and PM decreased. For 35% biodiesel, the composite NO_x emission increased by 0.97% while the composite particulate emission decreased by 26.13% relative to the reference diesel. The NO_x change is statistically significant at the 99% level. For the neat ester, the composite NO_x increased by 1.50% while PM was decreased by 66.0%. CO was reduced by 47.0% and total hydrocarbon by 43.8%. For the neat ester, the composite NO_x emission exceeded the 1991-1994 NO_x emission standard of 5 gm/bhp-hr NO_x . The composite PM emission met the 1994 standard of 0.1 gm/bhp-hr. Altitude does not increase NO_x emissions to a measurable effect. However, PM is typically increased by more than 1.5 times. The test engine is calibrated at low altitude for 0.25 gm/bhp-hr PM and typically emits 0.18 gm/bhp-hr. Thus, the 0.1 PM level with no aftertreatment from this engine is considered remarkable

A preliminary emissions model describing the effect of aromatics content, cetane number, and oxygen content has been developed by us in this report. The model allows prediction of how base diesel fuel properties should be changed for formulation of NO_x neutral biodiesel blends as compared to certification diesel fuel. Modest to substantial changes in aromatics content or cetane number should lead to NO_x neutral 20°/0 and 3 5°/0 biodiesel blends.

Engine efficiency was found to be the same for biodiesel and biodiesel blends as for the reference fuel. Fuel consumption for biodiesel blends can therefore be calculated from diesel fuel economy data.

2.0 TEST MATRIX AND FUELS

In the test program, four different biodiesel fuels were compared against a reference diesel fuel. The reference fuel was a commercial Number 2 diesel fuel which was obtained additive-free from the supplier. Biodiesel manufactured by Procter and Gamble was blended by weight to 20%, 35%, 65% and 100% levels. No analysis of the methyl soyester content of the biodiesel was obtained. However, the supplier, Interchem, indicated that the fuel was double distilled and the ester content of the biodiesel exceeded 99%.

All fuels were prepared gravimetrically by blending from single lots of the reference diesel with ester. Table 1 provides a summary of the fuels used in this study. The cetane numbers reported in Table 1 were measured for the actual blends by Core Laboratories in Houston, Texas. Other fuel analyses were conducted by Hauser Laboratories, Boulder, Colorado, including the biodiesel elemental analysis. Hauser determines chemical oxygen directly by oxidative coulometry. The oxygen content of blends was determined from the measured oxygen content of the two fuel stocks and the very accurately known weight percent of each stock in a given blend.

2.1 TEST MAP

The test matrix was carried out against the torque map for the diesel reference fuel. The map is used to generate the transient cycle commands. By using a single map, all measurements were made against an identical test cycle. Because of the greater energy density of diesel fuel, the engine is capable of generating both the greatest torque and greatest horsepower on the reference diesel at wide open throttle. Running other fuels on the diesel map would force them to perform from a load perspective as equal to diesel as possible. Because the blend fuels are lower in energy density, they will not generate the same wide open throttle power as Number 2 diesel, but can meet all intermediate load set points.

2.2 MAPPING CONDITIONS

The engine was mapped according to parameters provided by Detroit Diesel with a single exception. The rated idle speed for engine at sea level is 600 RPM. We found that the engine generated excessive hydrocarbon and particulate emissions due to misfire at this low idle speed. We elected to map at **650 RPM** for idle; this eliminated the emissions problem.

The engine was mapped at the nominal conditions in Table 2. Temperature and pressure settings are reported for the engine operating at rated speed and wide open throttle.

Prior to running each fuel, the engine was fully warmed and the map conditions were checked to insure that the engine operated on the fuel blend. No adjustments were made in the map parameters, however, since the reduced power generated on the other fuels results by necessity in lower pressures and temperatures. Importantly, the diesel map was checked several times to confirm that there was an insignificant performance change over the campaign for Number 2 diesel.

At the completion of the 20% biodiesel run, the Number 2 diesel map was inadvertently destroyed. The engine was remapped on Number 2 and the test program continued. The cycle performance between the first map and second map was compared and considered acceptably close (less than 10/0 in cycle work) so that the 20%/0 biodiesel blend was not rerun.

Table 3 presents a summary of map data for the various fuels at even speed increments. As Table 3 shows, the torque values at all speed ranges are a weak function of biodiesel content. Torque at wide open throttle appears to be increased at speeds near idle and reduced at higher speeds.

2.3 TEST RUNS

Table 4 shows the test plan for the program. Each blend tested was bracketed by a series of reference diesel tests. This protocol, while time consuming, provides for the ability to correlate emissions while engine drift is occurring. Drift is natural and may even be enhanced by the detergent action of oxygenates. The effect is small but very important for NO_x emissions since the NO_x change is on the order of 1% for the lower biodiesel concentrations.

**TABLE 1
FUEL ANALYSIS DATA**

BLEND COMPONENT DATA		
PROPERTY	DIESEL BASE	BIODIESEL
CARBON, WT%	86.64	77.22
HYDROGEN	12.80	11.56
OXYGEN	0.21	11.03
NITROGEN	0.11	
SULFUR	0.031	
FIA SATURATES, VOL%	64.4	
OLEFINS	1.3	
AROMATICS	34.3	
API GRAVITY	35.6	
IBP, F	387	
10"A	429	
50%	527	
90"A	632	
EP	677	

BLEND DATA

WT % BIODIESEL	WT % OXYGEN	CETANE NUMBER
0%	0.210/0	46.2
20 0/0	2.37	50.3
35%	4.00	52.2
65%	7.24	54.5
100%	11.03	56.4

**TABLE 2
MAPPING CONDITIONS**

IDLE SPEED	650 RPM
RATED SPEED	1800 RPM
CONDITIONS AT RATED SPEED AND WOT	
INTAKE PRESSURE	-16 INCHES WC
EXHAUST BACKPRESSURE	-32.5 INCHES WC
TURBO COOLER DP	40 INCHES WC
MANIFOLD AIR TEMPERATURE	112F

TABLE 3
MAP SUMMARY DATA FOR FUELS

TORQUE , FT-LBS

WT % BIODIESEL

RUN	1056	1071	1085	1111	1064	1105	1117	1091
	0%(REF)	0%(REF)	0%(REF)	0%(REF)	20%	35%	65%	100%
SPEED, RPM								
650	618	625	622	626	619	640	637	624
700	633	640	638	641	642	648	644	631
800	717	718	721	720	715	732	724	661
900	841	846	830	839	824	832	809	732
1000	969	965	971	970	971	978	973	802
1100	1136	1128	1118	1124	1123	1113	1096	1077
1200	1283	1279	1278	1286	1275	1270	1256	1210
1300	1251	1250	1240	1249	1236	1240	1222	1184
1400	1209	1214	1202	1208	1201	1194	1172	1134
1500	1168	1161	1155	1160	1145	1144	1125	1079
1600	1118	1112	1100	1110	1103	1097	1079	1042
1700	1051	1052	1038	1044	1040	1035	1011	985
1800	1014	1011	1003	999	993	991	974	940
1900	465	468	337	330	466	354	288	430

2.4 KEY TEST PARAMETERS

In actual transient testing, a number of variables besides speed and torque must be closely controlled to eliminate their effects on emissions.

TABLE 4
TEST PLAN MATRIX FOR BIODIESEL RUNS

FUEL	COLD RUN	HOT RUN
0%		3
20%	1	3
0%		3
100%	1	3
0%	1	3
35%	1	3
00/0	1	3
65%	1	3
0%		3

2.4.1. INTAKE HUMIDITY

Intake humidity affects emissions because increased water vapor results in increased heat capacity in the cylinder and thus lower temperatures at injection and during burning. We have measured the effect of humidity on emissions from this engine previously and confirmed the Code of Federal Regulations correction factor for low altitude performance. To minimize any humidity effect, all test runs were made as close to the EPA reference humidity of 75 grains water per pound of dry air as possible. Cast as a NO_x correction factor, the majority of the data were corrected for humidity by about +/- 1 %. The extreme correction was +3%. **All particulate data** were corrected to the reference humidity using the EMA correction factor which has also been shown by us in previous testing to be applicable at high altitude. While EPA does not recognize this correction for certification emissions, it is applied to insure that all emissions comparisons are made at constant engine test conditions.

2.4.2. INTAKE MANIFOLD

In on road applications, the Series 60 engine is equipped with an air-cooled aftercooler. For testing, the engine is supplied with a water-cooled exchanger. SAE procedure J-1937 describes the procedure to simulate on road intake manifold temperature as a function of load using a water cooled unit.

Intake air temperature after the turbocharger aftercooler depends on the turbocharger load and the cooling water temperature. The NO_x emission is dependent on the manifold temperature history over a test run. We establish the “proper” manifold

temperature behavior by providing 75 F \pm 2F (allowed range 68 to 86F) water to the turbo aftercooler. The coolant flow is set during mapping to achieve 1 12F at rated engine speed and wide open throttle. During each test run, the manifold temperature is allowed to swing between these limits based upon the local demand on the cooler.

2.4.3. FUEL TEMPERATURE

Fuel temperature can have an impact on NO_x emissions since fuel density and hence the power generated will vary with temperature. In our system, we control the fuel temperature via a fuel cooler so that a natural variation of about 10F occurs over the hot test (85 to 95 F). During cold start, the fuel is typically 75F until the fuel is warmed by engine heat loss. The maximum fuel temperature is adjusted during mapping at rated speed and wide open throttle at about 100F.

2.4.4. COLD START

For this engine, an oil temperature below about 70F causes the engine to start on cold assist. Since the transient test is run nominally at 77F but can be run between 68 and 86F, this is an important issue since emissions with cold assist may differ from emissions without assist. Thus, all cold runs are initiated with 75F to 77F oil to eliminate the cold assist function. In this program, the exception is the 20% biodiesel cold run which contained 24 seconds of cold assist operation. This may have produced slightly high PM, NO_x, CO and THC emissions for this cold run.

2.4.5. EMISSIONS CALIBRATION

During the entire test program, emissions were measured against the same set of span gases.

3.0 TEST DATA

3.1 RAW TEST DATA

Table 5 provides a summary of all test data collected during this study. The run number is a chronological marker which shows where in the campaign the run was conducted. The order of running was 20%, 100%, 3 5%, and 65% biodiesel. As previously mentioned, each fuel was bracketed using the reference.

Table 5 presents data on fuel consumption and carbon balances. The fuel data are the average of direct measurements made using a difference from a weigh cell and a totalized mass determined from a Micromotion mass flow meter respectively. The weigh cell accuracy is known to be better than 0. 5% of the fuel weight difference for a given transient test with the Series 60. The Micromotion meter is accurate to 0.3 5% of mass

TABLE 5
RAW EMISSION DATA SUMMARY, ALL FUELS

BASE DIESEL FUEL											
RUN #	TYPE	BHP-HR	GM/BHP-HR					CARBON BALANCE DATA			
			THC	NOX	c o	C O2	PM	LB/BHP-HR	CIN	CO/TEST	% DIFF
1112	COLD	22,259	0.172	5.011	5.357	578.64	0.325	0.404	7.785	7.864	-1.02%
1103	COLD	22,172	0.186	4.955	5.006	578.26	0.315	0.406	7.793	7.822	-0.37%
1059	HOT	22,366	0.150	4.576	4.224	550.15	0.295	0.385	7.468	7.494	-0.35%
1061	HOT	22,379	0.165	4.526	4.356	545.94	0.297	0.383	7.416	7.445	-0.39%
1063	HOT	22,335	0.155	4.591	4.333	549.84	0.300	0.385	7.451	7.482	-0.42%
1074	HOT	22,351	0.145	4.559	4.016	555.96	0.289	0.387	7.494	7.562	-0.97%
1081	HOT	22,299	0.127	4.638	4.174	555.85	0.278	0.391	7.564	7.546	0.24%
1088	HOT	22,234	0.128	4.593	4.136	557.40	0.294	0.398	7.668	7.544	1.62%
1090	HOT	22,274	0.130	4.552	4.118	557.93	0.291	0.396	7.650	7.564	1.12%
1098	HOT	22,237	0.131	4.585	3.894	566.56	0.280	0.387	7.460	7.663	-2.72%
1100	HOT	22,222	0.131	4.598	3.847	562.63	0.282	0.403	7.750	7.604	1.89%
1102	HOT	22,245	0.146	4.592	3.995	562.10	0.290	0.395	7.620	7.608	0.15%
1104	HOT	22,250	0.113	4.520	3.971	557.80	0.284	0.391	7.542	7.551	-0.12%
1114	HOT	22,295	0.120	4.573	3.950	558.20	0.281	0.393	7.598	7.571	0.35%
1115	HOT	22,262	0.136	4.598	4.028	560.47	0.287	0.393	7.585	7.593	-0.10%
1116	HOT	22,303	0.111	4.579	3.958	557.79	0.281	0.392	7.577	7.568	0.12%
HOT AVERAGE		22,290	0.135	4.577	4.071	557.04	0.288	0.391	7.560	7.557	0.03%
HOT STANDARD DEVIATION		0.052	0.016	0.031	0.157	5.46	0.007	0.006			
COMPOSITE			0.141	4.635	4.230	560.10	0.292	0.393	7.593	7.598	-0.07%
20% BIODIESEL											
1065	COLD	22,703	0.216	5.044	5.787	569.35	0.322	0.414	7.976	7.906	0.88%
1068	HOT	22,341	0.121	4.600	3.746	548.80	0.243	0.394	7.459	7.456	0.04%
1069	HOT	22,336	0.123	4.640	3.810	549.95	0.247	0.394	7.467	7.471	-0.06%
1070	HOT	22,368	0.129	4.646	3.846	553.06	0.249	0.396	7.509	7.525	-0.21%
HOT AVERAGE		22,348	0.124	4.629	3.801	550.60	0.246	0.395	7.478	7.484	-0.08%
HOT STANDARD DEVIATION		0.017	0.004	0.025	0.051	2.20	0.003	0.001			
COMPOSITE			0.138	4.688	4.084	553.28	0.257	0.398	7.549	7.544	0.06%

TABLE 5 CONTINUED
35% BIODIESEL

RUN #	TYPE	BHP-HR	GM/BHP-HR					CARBON BALANCE DATA			
			THC	NOX	c o	C02	PM	LB/BHP-HR	LB/TEST	CIN	% DIFF
1106	COLD	22.119	0.166	5.008	4.479	577.95	0.247	0.420	7.751	7.787	-0.46%
1108	HOT	22.260	0.117	4.604	3.231	556.34	0.213	0.403	7.468	7.519	-0.68%40
1109	HOT	22.228	0.115	4.629	3.238	556.13	0.208	0.393	7.318	7.506	-2.56%
1110	HOT	22.214	0.102	4.642	3.191	558.41	0.201	0.407	7.534	7.530	0.05%40
HOT AVERAGE		22.234	0.111	4.625	3.220	556.96	0.207	0.401	7.440	7.518	-1.06%
HOT STANDARD DEVIATION		0.023	0.008	0.019	0.025	1.26	0.006	0.007			
COMPOSITE			0.119	4.680	3.400	559.96	0.213	0.404	7.484	7.557	0.98%40

65% BIODIESEL

1118	COLD	22.068	0.141	5.198	3.851	580.47	0.199	0.439	7.802	7.788	0.18%
1120	HOT	22.136	0.073	4.758	2.748	557.84	0.149	0.421	7.500	7.485	0.20%
1121	HOT	22.130	0.093	4.820	2.714	558.02	0.151	0.421	7.508	7.486	0.30%
HOT AVERAGE		22.133	0.083	4.789	2.731	557.93	0.150	0.421	7.504	7.486	0.25%
HOT STANDARD DEVIATION			0.015	0.043	0.024	0.128	0.002	0.000			
COMPOSITE			0.091	4.848	2.891	561.15	0.157	0.424	7.547	7.529	0.24%

100% BIODIESEL

1092	COLD	21.887	0.112	5.525	2.938	587.66	0.119	0.455	7.691	7.799	-1.41%
1094	HOT	21.921	0.052	5.087	1.936	568.86	0.080	0.441	7.467	7.540	-0.98%
1095	HOT	21.960	0.090	5.115	2.237	568.11	0.107	0.441	7.483	7.551	-0.91%
1096	HOT	21.935	0.078	5.115	2.196	570.34	0.100	0.439	7.440	7.571	-1.76%
HOT AVERAGE		21.939	0.073	5.106	2.123	569.10	0.096	0.441	7.463	7.554	-1.22%
HOT STANDARD DEVIATION		0.020	0.019	0.016	0.163	1.14	0.014	0.001			
COMPOSITE			0.079	5.166	2.239	571.75	0.099	0.443	7.496	7.589	-1.24%

flow except at idle where errors of 4% are possible. From these two measurements, the maximum expected fuel error is thus under 10/O.

Based upon the analytical data in Table 1, the H/C ratio of the base diesel and biodiesel are 0.148 and 0.150 respectively. Thus, the heating value of the blend should be to a very good approximation a linear function of fuel oxygen content. The fuel consumption was regressed against weight percent oxygen in the fuel. The best fit was found to be:

$$\text{BSFC} = 0.386 + 0.00482 \cdot \text{WT\% OX}$$

The standard error of the regression is 0.8% of the maximum fuel consumption which is equivalent to the expected fuel error. Since the fuel consumption is proportional to the fuel heating value, it is concluded that the engine efficiency is the same for biodiesel and biodiesel blends as for the reference fuel. It is concluded that for the Series 60 engine, the fuel consumption for biodiesel blends is directly calculable from diesel fuel economy data.

The carbon balances in Table 5 were closed using the analytical data for the fuels in Table 5, the total fuel consumption for a given test, and the emissions for CO₂, CO, THC, and PM for a given test. PM was assumed to be 100% carbon and total hydrocarbon was assumed to be the same as diesel fuel. No change in response for oxygenated fuels was used in the hydrocarbon measurement and no correction was made to the hydrocarbon for oxygen content. If the hydrocarbon in the exhaust is oxygenated, its total mass might be underestimated. The carbon balance closure is generally within 1 %. This substantiates the fuel consumption estimates and demonstrates that no substantial systematic errors exist in the emission measuring

The data in Table 5 were recast into Table 6 to provide average hot and composite test emissions for each fuel. The composite emissions were determined by weighting the cold average by 1/7 and the hot average by 6/7 according to the Code of Federal regulations. In all cases, NO_x and PM emissions were corrected for humidity using the following corrections:

$$\text{NO}_x \text{ FACTOR} = 1/(1 - 0.0026 \cdot (H - 75))$$

$$\text{PM FACTOR} = 1/(1 + 0.0017 \cdot (H - 75))$$

where H is the absolute intake air humidity in grams water per pound of dry air,

Table 7 presents the change in emissions for biodiesel addition as a function of biodiesel content. Except for NO_x, biodiesel effectively reduces regulated emissions. Up to 35% biodiesel, the NO_x change appears to be on the order of 10%. Beyond 35% biodiesel, the NO_x increases rapidly to more than 1% for neat biodiesel.

TABLE 6
SUMMARY OF RESULTS, RAW DATA

	FUEL, PERCENT BIODIESEL				
	0% (REF)	20.00%	35.00%	65.00%	100.00%
THC Cold	0.179	0.216	0.166	0.141	0.112
THC Hot	0.135	0.124	0.111	0.083	0.073
THC Composite	0.141	0.138	0.119	0.091	0.079
NOx Cold	4.983	5.044	5.008	5.198	5.525
NOx Hot	4.577	4.629	4.625	4,789	5.106
NOX Composite	4.635	4.688	4.680	4.848	5.166
CO Cold	5.182	5.787	4.479	3.851	2.938
CO Hot	4.071	3.801	3.220	2.731	2.123
CO Composite	4.230	4.084	3.400	2.891	2.239
C02 Cold	578.45	569.35	577.95	580.47	587.66
C02 Hot	557.04	550.60	556.96	557.93	569.10
C02 Composite	560.10	553.28	559.96	561.15	571.75
PM Cold	0.320	0.322	0.247	0.199	0.119
PM Hot	0.288	0.246	0.207	0,150	0.096
PM Composite	0.292	0.257	0,213	0.157	0,099

**TABLE 7
SUMMARY OF RESULTS, RAW DATA**

	FUEL, PERCENT BIODIESEL			
	20.00%	35.00%	65.00%	100.00%
THC Cold	20.88%	-7.30% ⁴⁰	-21.26%	-37.45% ⁰
THC Hot	-7.69%	-17.70%	-38.46%	-45.87%
THC Composite	-2.51%	-15.71%	-35.54%	-44.04%
NOx Cold	1.22%	.50%	4.32%	10.88% ⁴⁰
NOx Hot	1.12%	1.05%	4.63%	11.55%
NOx Composite	1.14%	.97%	4.58%	11.45%
CO Cold	11.68%	-13.56%	-25.68%	-43.30% ⁷⁰
CO Hot	-6.65%	-20.91%	-32.92%	-47.86%
CO Composite	-3.44% ⁹⁴⁰	-19.62%	-31.65%	-47.06%
C02 Cold	-1.57%	-.09%	.35%	1.59%
C02 Hot	-1.16%	-.01%	.16%	2.16%
C02 Composite	-1.22% ⁴⁰	-.03%	.19%	2.08%
PM Cold	.70%	-22.63%	-37.79%	-62.67% ⁷⁰
PM Hot	-14.39% ⁴⁰	-28.02%	-47.87%	-66.81%
PM Composite	-12.03%	-27.18%	-46.30%	-66.16%

Over the course of testing, there was an observed emissions drift as determined from the reference fuel emission data. In order to estimate the impact of drift on the emissions, the hot emissions for the reference fuel were regressed against test number which was used as a surrogate for test time. The data were corrected to zero time (run 1059) by the following linear equations, whose coefficients are presented in Table 8.

$$\text{ADJUSTED/RAW} = 1/(1 + A(\text{RUN\#} - 1059))$$

TABLE 8
TIME CORRECTION OF TEST DATA

EMISSION	A	R SQUARED
THC	-3.943 E-3	0.591
NO _x	o	0.014
c o	-1.479E-3	0.654
C02	3.784E-4	0.587
PM	-8 166 E-4	0.477

The regression results show that all emissions except for NO_x showed a small drift. In the case where drift was evident, the regression was able to account for about 50% of the variation in the data. The remainder of the unexplained variation is most likely experimental error. Figures 1 through 5 show emission trends as a function of time. Figures 6 through 10 show the regression results. Table 9 and Table 10 present the summary of corrected emissions and the percentage change in emissions as a function of oxygen content. Figures 11 through 14 show plots of emissions as a function of oxygen content.

3.2 DISCUSSION

In this section, all discussion applies to the time corrected data. Figures 6 through 10 present the results of a linear model least squares analysis of the test data for the reference diesel fuel. In the regression, data were first normalized against the emissions for run 1059. The normalized reference diesel emission data were then fit against (run number - 1059) with a forced intercept of unity. All data were corrected to the zero time (run 1059) emissions.

Table 9 summarizes the emissions data. For diesel engines, the two most important emissions are NO_x and PM. The data clearly demonstrate the NO_x-PM tradeoff; reducing PM in a given engine configuration often raises NO_x. For neat biodiesel, the NO_x emission exceeds 5 g/bhp-hr, an increase of 0.53 g/bhp-hr over the reference fuel. The PM level is simultaneously reduced by 0.198 g/bhp-hr to a level equal to the 1994 truck engine standard. SOF determinations were not made. However, the particulate appeared to be composed of a significant portion of oils which suggests that a SOF oxidation catalyst could be even more effective in particulate control.

TABLE 9

SUMMARY OF RESULTS, TIME CORRECTED DATA

	FUEL, PERCENT BIODIESEL				
	0% (REF)	20.0070	35.00%	65.00%	100.0070
THC Cold	0.222	0.222	0.204	0.184	0.129
THC Hot	0.154	0.130	0.139	0.110	0.085
THC Composite	0.164	0.143	0.148	0.120	0.092
NOx Cold	4.983	5.044	5.008	5.198	5.525
NOx Hot	4,577	4,629	4.625	4.789	5.106
NOX Composite	4.635	4.688	4.680	4.848	5.166
CO Cold	5.584	5.838	4.814	4.219	3.089
CO Hot	4.270	3.858	3.477	3.005	2.242
CO Composite	4.458	4.141	3.668	3.178	2.363
C02 Cold	568.03	568.06	567.85	567.79	580.42
C02 Hot	550.51	548.53	546.62	545.24	561.46
C02 Composite	553.01	551,32	549.65	548.46	564,16
PM Cold	0.333	0.324	0.257	0.209	0.123
PM Hot	0.295	0.248	0.216	0,158	0.098
PM Composite	0.300	0.259	0.222	0.165	0.102

TABLE 10

EMISSION DIFFERENCES, PERCENT, TIME CORRECTED DATA

	FUEL, PERCENT BIODIESEL		
	20.00%	35.00%	65.00%
THC Cold			100.00%
THC Hot	.09%	-7.97%	-41.76%
THC Composite	-15.78%	-9.87%	-44.77%
	-12.71%	-9.50%	-43.75%
NOx Cold	1.21%	.50%	10.88%
NOx Hot	1.13%	1.05%	11.56%
NOx Composite	1.14%	.97%	11.46%
CO Cold	4.56%	-13.79%	*4.68%
CO Hot	-9.66%	-18.56%	*7.49%
CO Composite	-7.11%	-17.71%	*6.99%
CO2 Cold	.01%	-.03%	2.18%
CO2 Hot	-.36%	-.71%	1.99%
CO2 Composite	-.31%	-.61%	2.02%
PM Cold	-2.81%	-22.73%	-63.06%
PM Hot	-15.77%	-26.77%	-66.78%
PM Composite	-13.72%	-26.13%	-66.05%

Table 10 shows the emissions changes in percent from the reference fuel. Figures 11 through 14 show these data graphically. Except for NO_x , the regulated emissions are reduced proportionally to the oxygen content. The NO_x emission is curved upward; the change in NO_x at 20% and 35% biodiesel is on the order of 10%. Between 35% and 100% the NO_x increases rapidly; at 65%, the NO_x is increased by 4.6% while for neat biodiesel, the emission is increased by 11.5%.

Table 11 shows the results of a test for the difference between NO_x emissions for 20% and 35% biodiesel blends compared to the reference diesel. In both cases, the observed NO_x increase for the blends is statistically significant at about the 0.01 level (99% confidence) based upon a student-t analysis. This means that the increased NO_x emission observed for biodiesel blends is most likely real.

In other fuel work conducted at CIFER, we have found that certain fuel properties impact emissions proportionally the same at high altitude as at low altitude. Specifically, the effects of aromatic content and cetane number for the Series 60 engine track results obtained by Unman, et al. (1990) and Nikanjam (1993). The proportional changes observed in this study for lower biodiesel blends seem to agree with low altitude data gathered from a variety of sources by the National Soy Diesel Board (NSDB).

An interesting result is the apparent low sensitivity of NO_x emissions to biodiesel amounts to 35% by weight. At the 35% level, the particulate reduction is large enough to offer significant emission benefits to fleet operators at little or no NO_x penalty. Additionally, the NO_x emission change is small enough that it could be treatable with cetane enhancing additives or by adjusting the aromatic content of the base fuel.

3.3 PRELIMINARY EMISSIONS MODEL

Table 12 presents results from the CRC VE-I (Unman, et al., 1990) study for a wide range of fuels in which cetane number and aromatic content were varied using Series 60 technology. The fuels did not contain significant levels of oxygen. We have verified this model on the engine used in this study against a series of aromatic fuels ranging from 8.8% to 35% aromatics and only a narrow range of natural cetane numbers (45 to 47.5) at high altitude for both NO_x and PM. Since the base emissions for our engine at altitude are different than those reported by SWRI, the comparison is made on a relative basis; that is, we have demonstrated that the effect of fuel changes on emissions are proportionally correct.

In order to estimate the effect of key fuel property changes on emissions of NO_x and PM, we have extended the SWRI model for oxygen content. (Additional data are required to verify the model.) The purpose of extending the model is to estimate the effect of blending stock properties on emissions of fuels containing biodiesel. The hypothesis posed is the following: how should base fuel properties be changed to produce a NO_x neutral fuel compared to diesel certification fuel?

Table 11

Statistical Analysis for NO_x Increase Due to Biodiesel for Hot Runs

	% Biodiesel		
	0	20	35
$\langle \text{NO}_x \rangle$	4.577	4.629	4.625
δ		+0.052	+0.048
s	0.031	0.025	0.019
n	14	3	3
σ^2_{pooled}		0.00092	0.00088
n_{pooled}		2.47	2.47
$(\sigma/\sqrt{n})_{\text{pooled}}$		0.0193	0.0189

null hypothesis $\mu_B - \mu_R = 0$ alternative hypothesis $\mu_B - \mu_R > 0$

t	2.694	2.539
$t_{0.95}$	1.753	1.753
$t_{0.99}$	2.602	2.602

Reject null hypothesis. NO_x increase is real. If $t > t_{\alpha}$ reject null hypothesis and conclude emission increase is real.

 $\langle \text{NO}_x \rangle$ = average NO_x δ = difference in averages

s = standard deviation

n = number of data points

 σ = variance μ = true mean

B = biodiesel

R = reference diesel

TABLE 12

**GENERALIZED MODELS FOR ESTIMATING TRANSIENT EMISSIONS
FROM A 1991 PROTOTYPE DDC SERIES 60 (60-11-330)
USING FIA AROMATICS, ALONG WITH TOTAL AND BASE CETANE NUMBERS**

Log_e Cold-Start Emissions^c	Intercept	FIA Aromatics		LBCET35^a		LDCET35^b		R^{2d}
		Coeff.	P-Value	Coeff.	P-Value	Coeff.	P-Value	
LMHC	2.138 E-1	--	--	-7.112E-1	0.0001	-6.879E-1	0.0001	0.881
LMCO	1.381	--	--	-3.180E-1	0.0001	-3.000E-1	0.0001	0.951
LNOX	1.814	03.005E-3	0.0001	-2.438E-2	0.0151	--	--	0.460
LPART	-1.534	--	--	-1.368E-1	0.0001	-1.306E-1	0.0030	0.517

Log_e Hot-Start Emissions^c	Intercept	FIA Aromatics		LBCET35^a		LDCET35^b		R^{2d}
		Coeff.	P-Value	Coeff.	P-Value	Coeff.	P-Value	
LMHC	1.156	--	--	-1.004	0.0001	-9.434E-1	0.0001	0.944
LMCO	1.508	--	--	-4.227E-1	0.0001	-4.302E-1	0.0001	0.980
LNOX	1.566	2.619E-3	0.0001	-5.443E-2	0.0001	-3.968E-2	0.0014	0.641
LPART	-1.355	3.190E-3	0.0283	-2.013E-1	0.0001	-1.377E-1	0.0009	0.719

Log_e Composite Emissions^c	Intercept	FIA Aromatics		LBCET35^a		LDCET35^b		R^{2d}
		Coeff.	P-Value	Coeff.	P-Value	Coeff.	P-Value	
LMHC	1.046	--	--	-9.718 E-1	0.0001	-9.153 E-1	0.0001	0.940
LMco	1.49Q	--	--	-4.072E-1	0.0001	-4.100E-1	0.0001	0.977
LNOX	1.604	2.693E-3	0.0001	-4.867E-2	0.0001	-3.217E-2	0.0066	0.606
LPART	-1.390	2.812E-3	0.0323	-1.897E-1	0.0001	-1.360E-1	0.0003	0.751

^aLBCET35 is Log_e (Base Cetane - 35).

^bLDCET35 is Log_e (Total Cetane - 35) - Log_e (Base Cetane - 35).

^cEstimated emission (g/hp-hr) = e^x ; where $x = \text{Log}_e \text{ Emission Intercept} + a (\text{FIA, \%}) + b (\text{LBCET 35}) + c (\text{LDCET35})$, and "e" = 2.71828.

^dR² terms when test time adjustment is transferred to the intercept.

In producing a model, the following steps were followed:

1. The trends predicted by VE-I for NO_x and PM were assumed correct
2. The emissions for the aromatic and cetane numbers of our test fuels were calculated using VE-I.
3. The model was adjusted to properly predict the emission of our diesel reference fuel.
4. The additional emission due to oxygen was determined and correlated against fuel oxygen content.

Figures 15 and 16 show the regression data for NO_x and PM, While the NO_x fit is better, the overall predictive power of both models is adequate to investigate the impact of fuel changes on NO_x and PM emissions. Table 13 summarizes the model.

Table 13
Model Coefficients for Oxygenated Fuels
Hot Run Emissions

$$\text{Ln Emission} = A + B (\% \text{ aromatics}) + C \text{Ln}(\text{CN\#}-35) + D (\% \text{ oxygen})$$

	NO _x	PM
A	1.56264	-0.84387
B	2.619 E-3	3.19 E-3
c	-5.440 E-2	-2.01 E-1
D	0.02061	-0.07147
R* (adjusted)	0.737	0.715
Std error	0.010	0.064

For the biodiesel data, the model predicts NO_x emissions to $\pm 1\%$. Particulate are predicted to $\pm 5\%$.

Using the model, aromatics were varied at fixed cetane number and cetane number was varied at fixed aromatic content to produce a NO_x neutral fuel. The impact on PM emission was also calculated. The reference fuel for NO_x neutrality comparison was the base diesel used in this study.

Table 14 shows that for B-20, a NO_x neutral fuel could be made by reducing the aromatic content of the base about 4.6% relative to the certification fuel aromatic content. Alternately, the natural cetane number of the base could be raised by 6.6 units. There is some data from the VE-I study (Ullman, et al., 1990) that indicates the impact of natural cetane number on emissions is greater than the impact of improved cetane number using 2-Ethylhexylnitrate cetane improver. The treated cetane number would have to be increased at least by this amount. The particulate model predicts a greater PM reduction than with biodiesel alone.

In the case of 35% biodiesel, the fuel would be NO_x neutral if the aromatic content was lowered by about 13.5% or the base cetane number was raised by 18.1 units. In this case, PM changes are much greater than 25% relative to the base fuel also,

Table 14
Predicted Property Changes to Produce a NO_x Neutral Biodiesel Blend

<u>% Biodiesel</u>	<u>Δ% Aromatics in Base (level)</u>	<u>ACN in Base (level)</u>	<u>APM %</u>
20%	-4.6 (29.7)	O (46.2)	-22%
	o (34.3)	+6.6 (52.8)	-24%
35% ⁴⁰	-13.5% (20.8)	O (46.2)	-35%
	o (34.3)	+18.1 (64.3)	-38% ⁴⁰

3.4 APPLICABILITY

Biodiesel blends and neat biodiesel are potentially applicable in three areas:

1. On-road urban bus retrofits,
2. On-road general use
3. Off-road.

The on-road urban bus retrofit criteria which biodiesel blends best fit is the 25% PM reduction criteria. To be most widely applicable, such fuels should be NO_x neutral relative to certification fuel although strictly speaking this appears to not be required.

For general on-road use, biodiesel blends will have to be proven NO_x neutral as a part of the diesel fuel waiver process.

Under EPA's substantially similar rule currently in development for diesel fuels, oxygenated diesels will require a fuel waiver. A key element of such a waiver is that any such fuel be equivalent to (or better) than diesel certification fuel when examining each regulated emission. For oxygenates in general, and especially for biodiesel, NO_x emissions are found to increase when compared to the fuel base stock to which the oxygenate is blended. A subset of fuel should be found with base stocks such that the NO_x emission of the blend is equivalent to certification fuel as the empirical model in the previous section attempted to demonstrate.

For off-road use, EPA is currently developing a certification test related to NO_x and opacity. While no rules currently exist for off-road fuels, future rulemaking could include NO_x control for off-road fuels.

It is concluded that NO_x neutrality will be important to the use of biodiesel in most applications

To that end, we propose three areas of future work directed at better understanding the relationship between fuel composition and emissions in the Series 60 engine.

4.0 FUTURE WORK

The results of this brief study suggest several avenues of future work

- 1 Examine the effect of varying aromatic content and natural cetane number of the base fuel on emissions for fuels blended with biodiesel to validate the model and prove that NO_x neutral fuels can be produced as compared to certification.
- 2 Examine the effect of different oxygenates with widely differing cetane numbers (and possibly boiling points), i.e. biodiesel produced from different feedstocks, including waste oils, to determine whether cetane enhancement due to oxygenates is effective in NO_x emission control. This study would further expand the fuel model by generalizing it for oxygenates and assist in introducing oxygenates generally into the marketplace.
- 3 Examine response of biodiesel blend fuels with various NO_x additives, particularly cetane improvers at various base fuel quality levels (aromatics and CN), to establish the NO_x and PM response to cetane improvers in the presence of oxygen.

5.0 REFERENCES

Nikanjam, M., Development of the First CARB Certified California Alternative Diesel Fuel, Chevron Research, SAE 930728, March, 1993.

Unman, T., Mason, R., Montalvo, D., Study of Cetane Number and Aromatic Content Effects on Regulated Emissions from a Heavy-Duty Engine, SWRI, CRC Contract YE-1, September, 1990.

FIGURE 1 RUN NUMBER VRS THC FOR NREL REFERENCE DIESEL RUNS

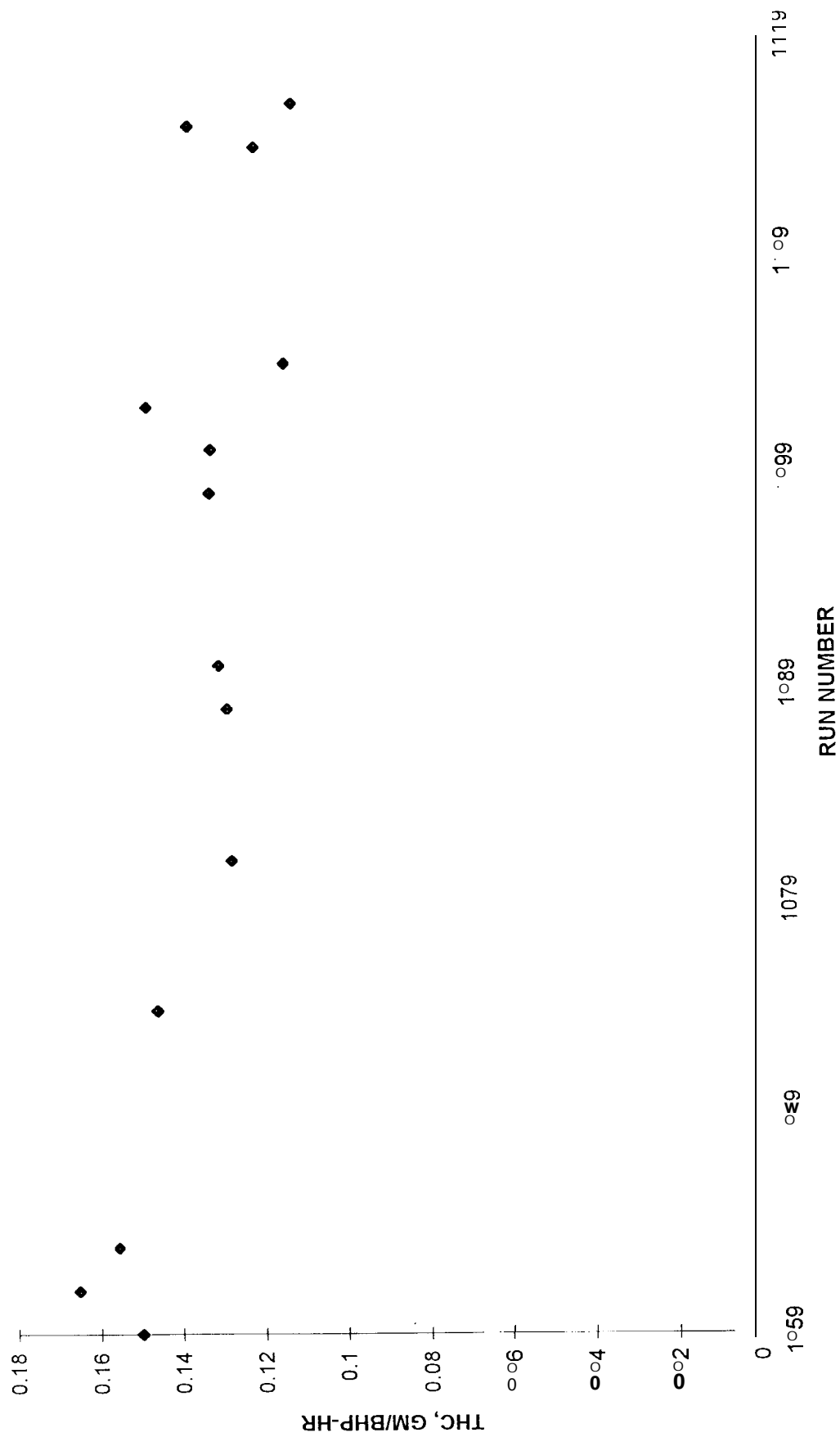


FIGURE 2 Run Number vs NOX for NREL Reference Diesel Runs

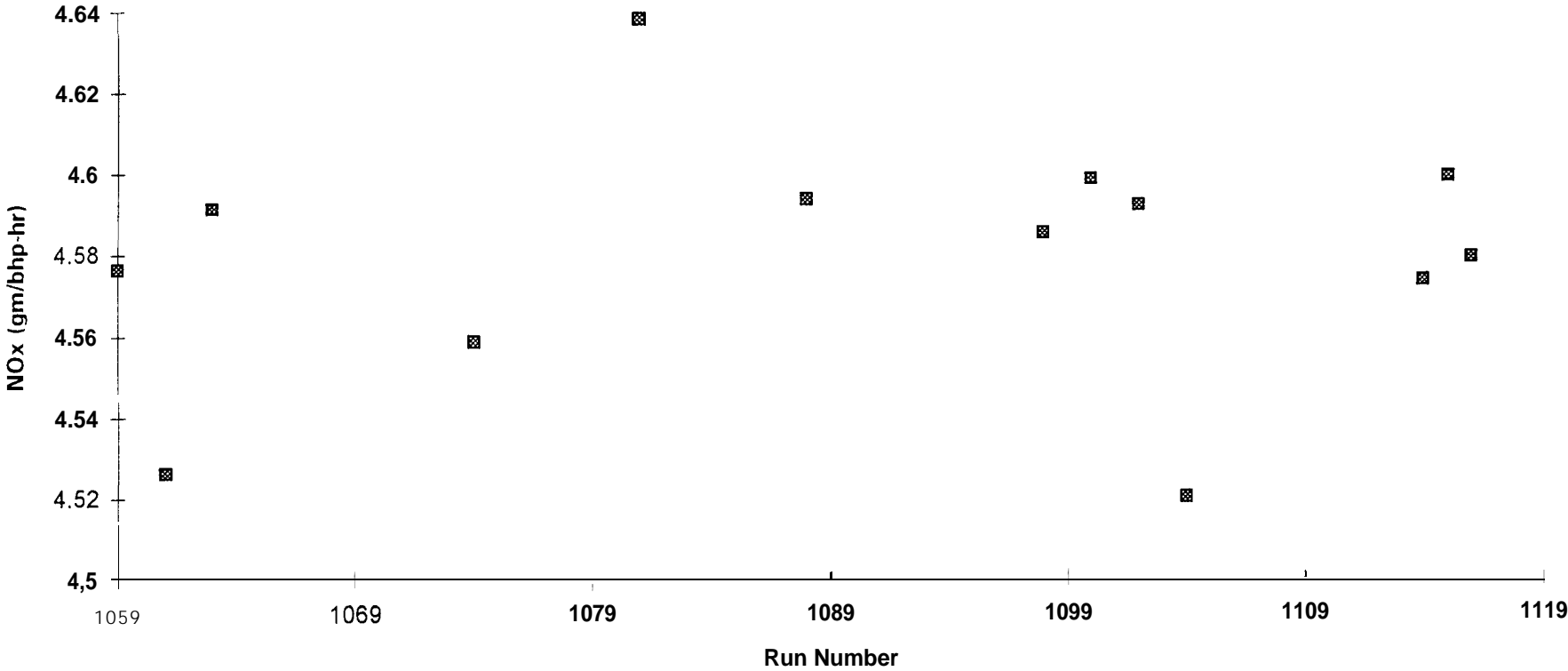


FIGURE 3 Run Number vs CO Emissions for NREL Reference Diesel

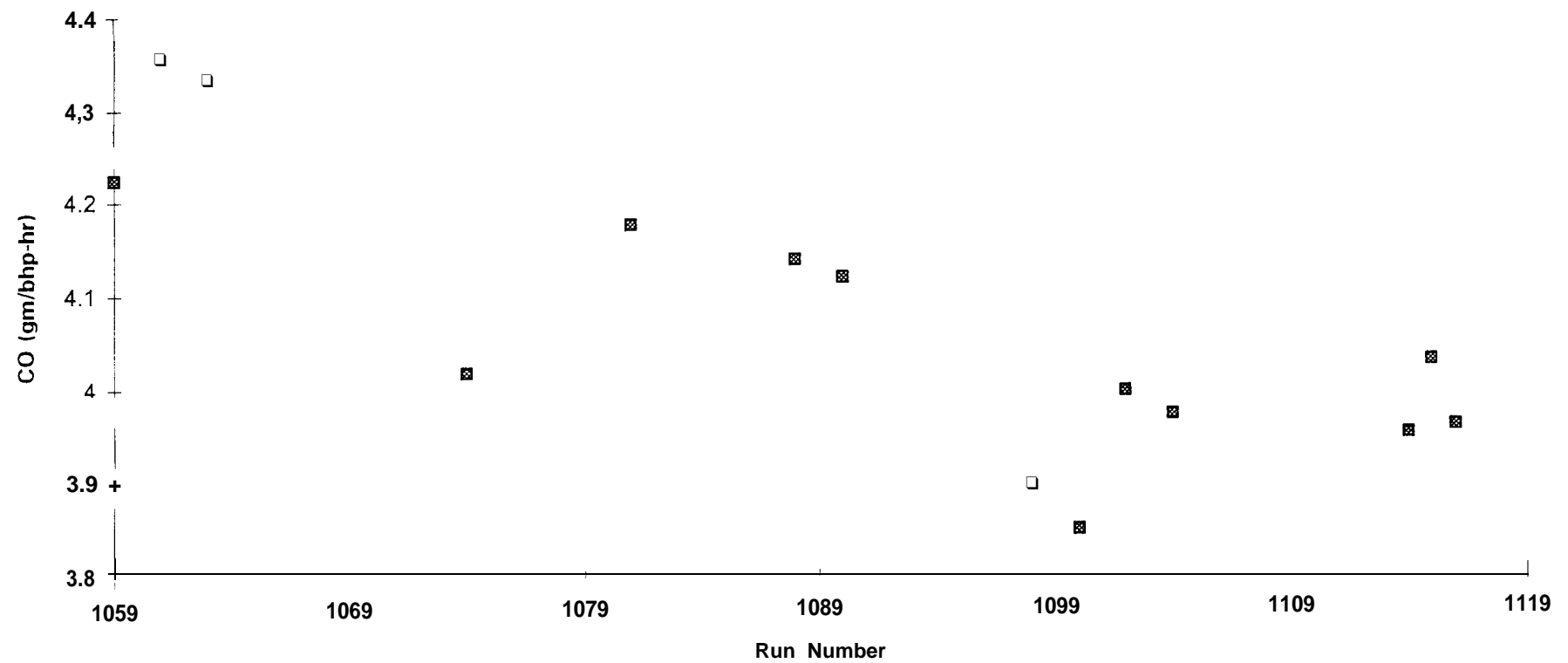


FIGURE 4 Run Number vs CO2 Emissions for NREL Reference Diesel

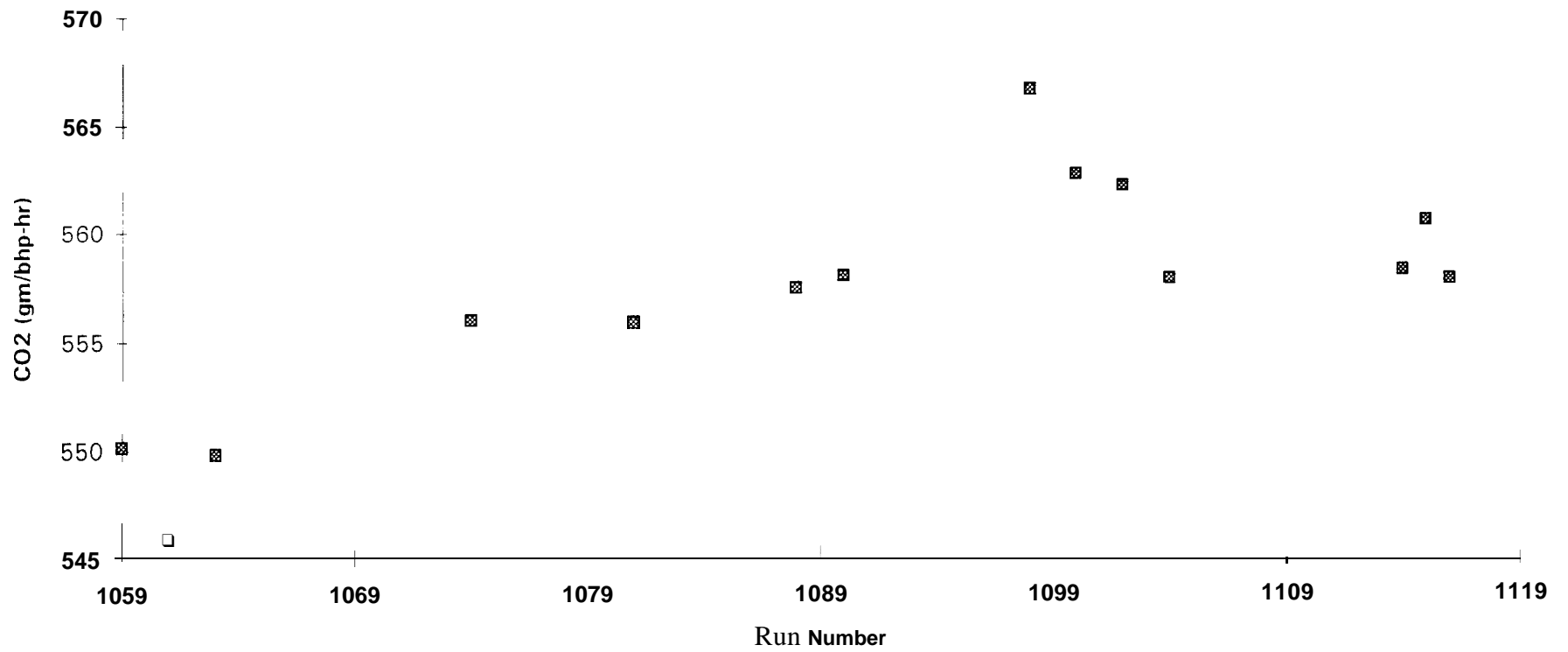


FIGURE 5 Run Number vs PM for NREL Reference Diesel

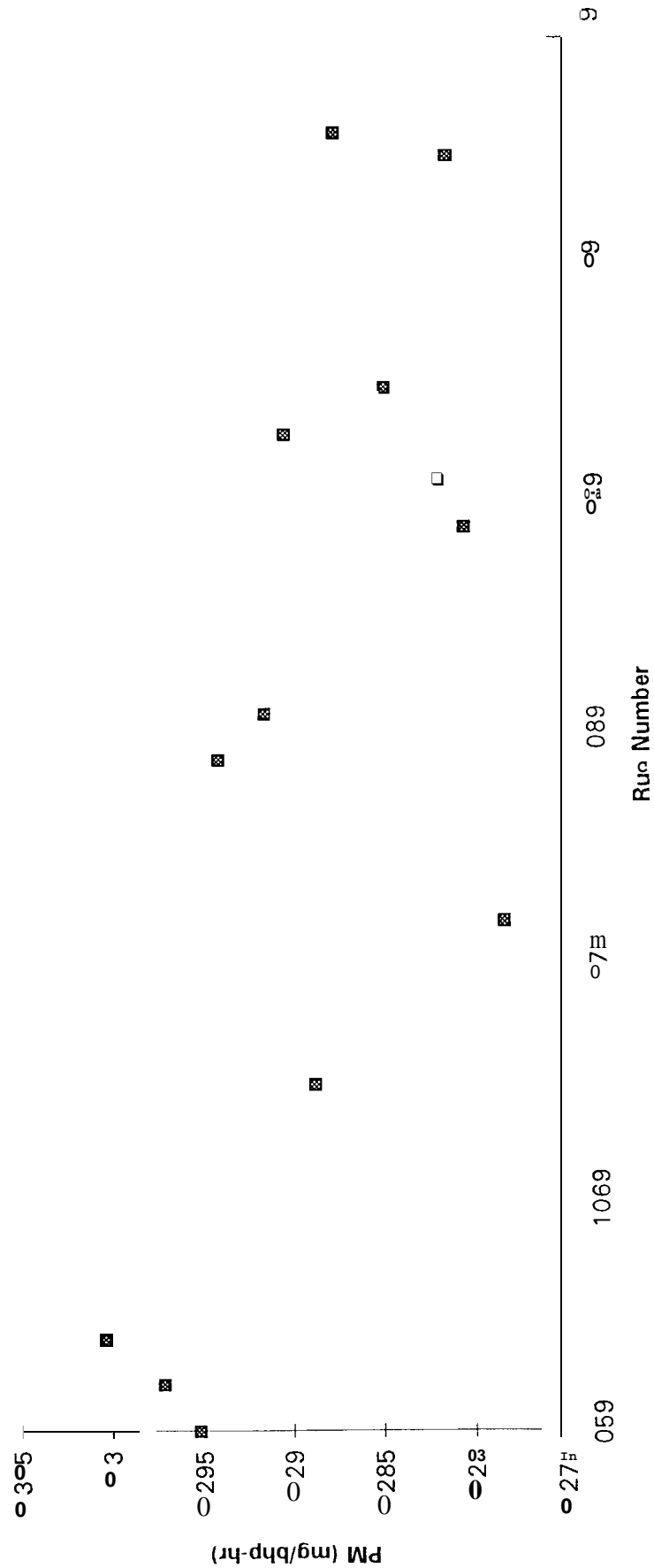


FIGURE 6 THC CORRECTION PLOT

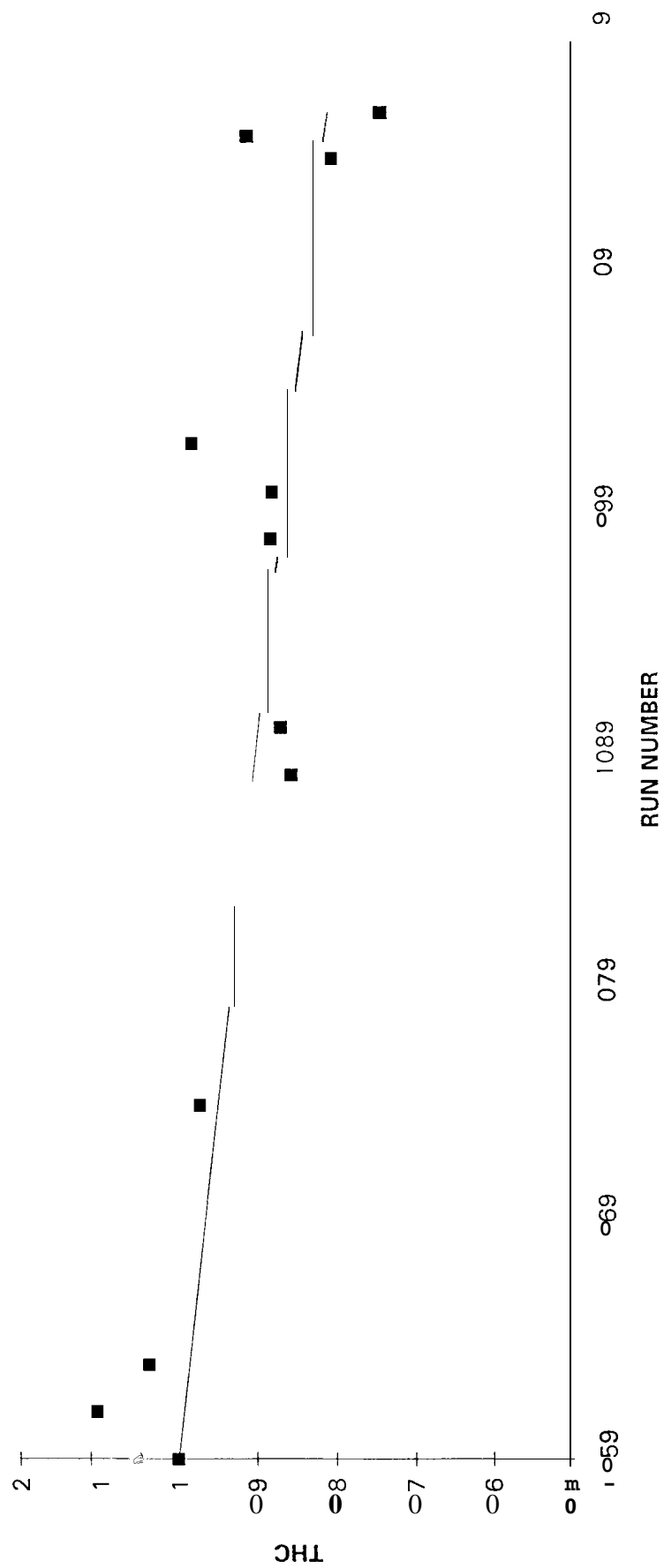


FIGURE 7 NOx Correction Plot

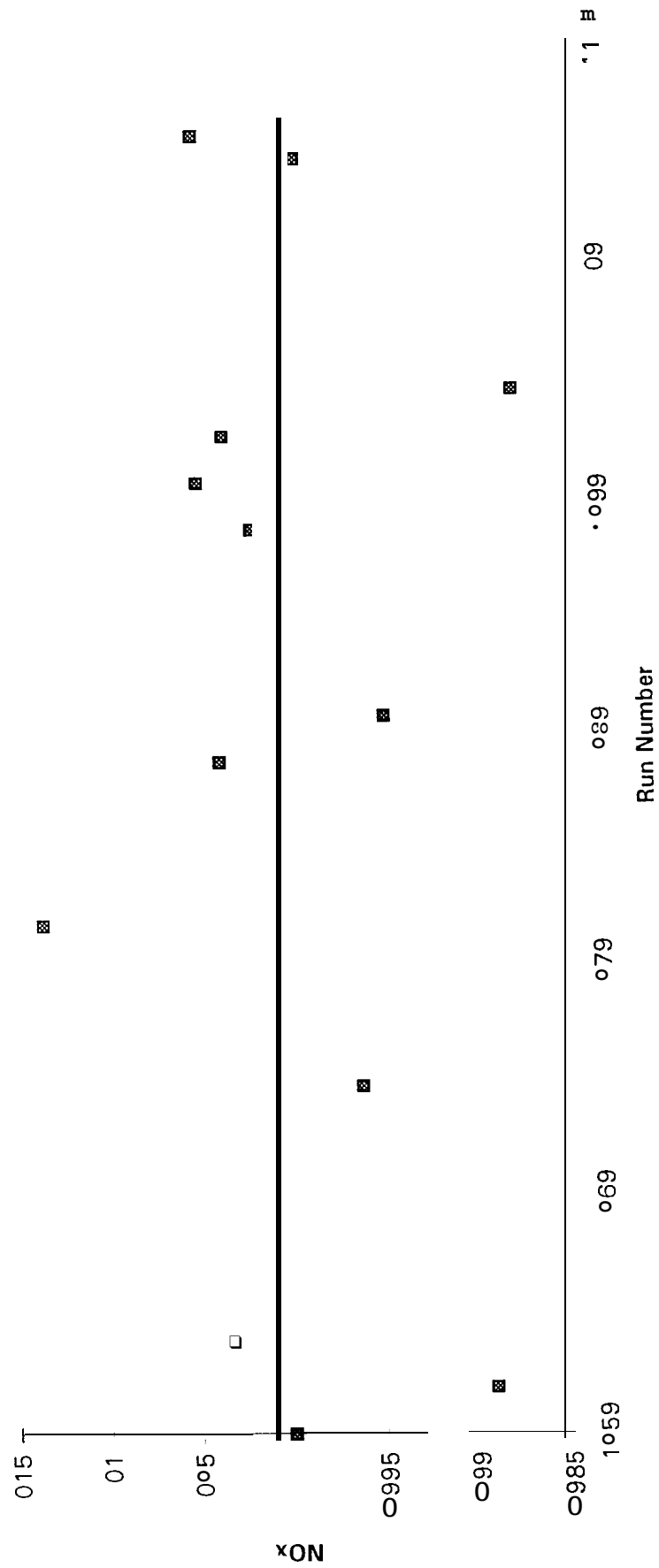


FIGURE 8 CO Correction Plot

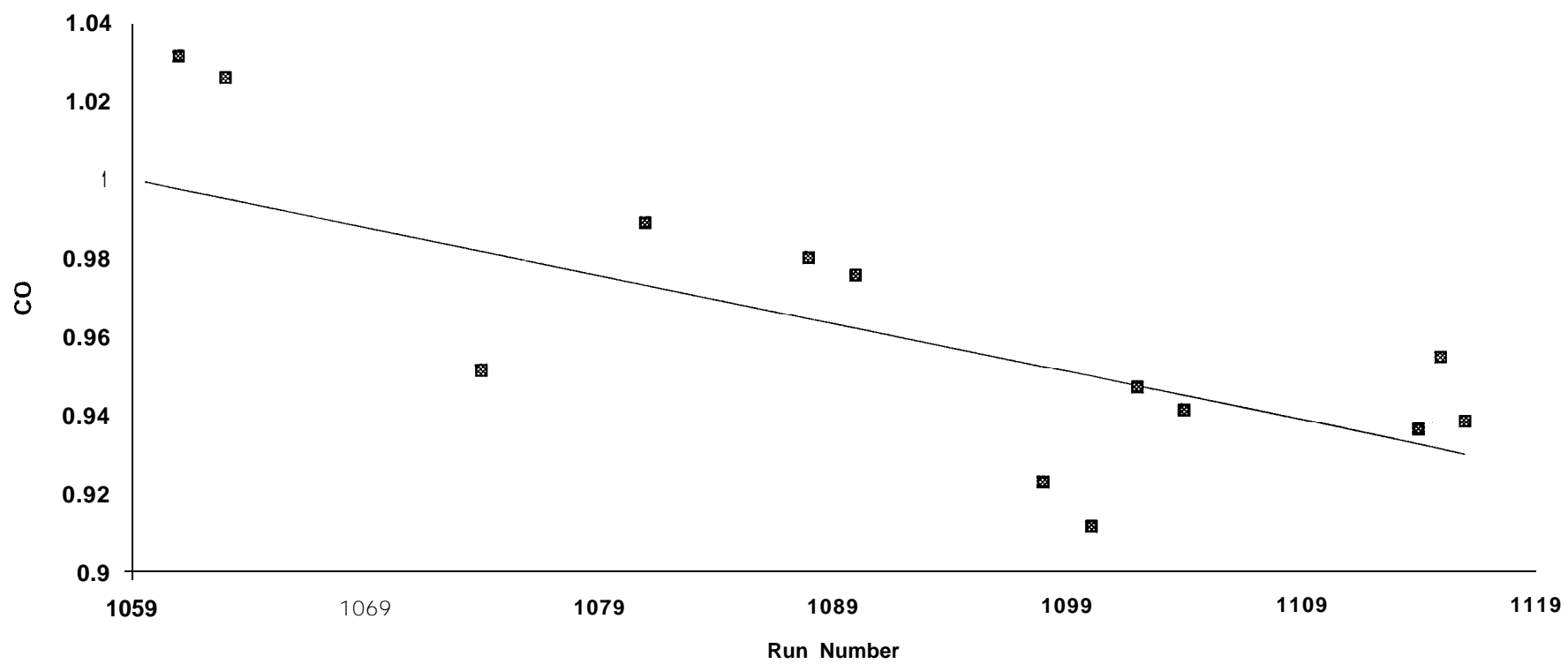


FIGURE 9 CO2 Correction Plot

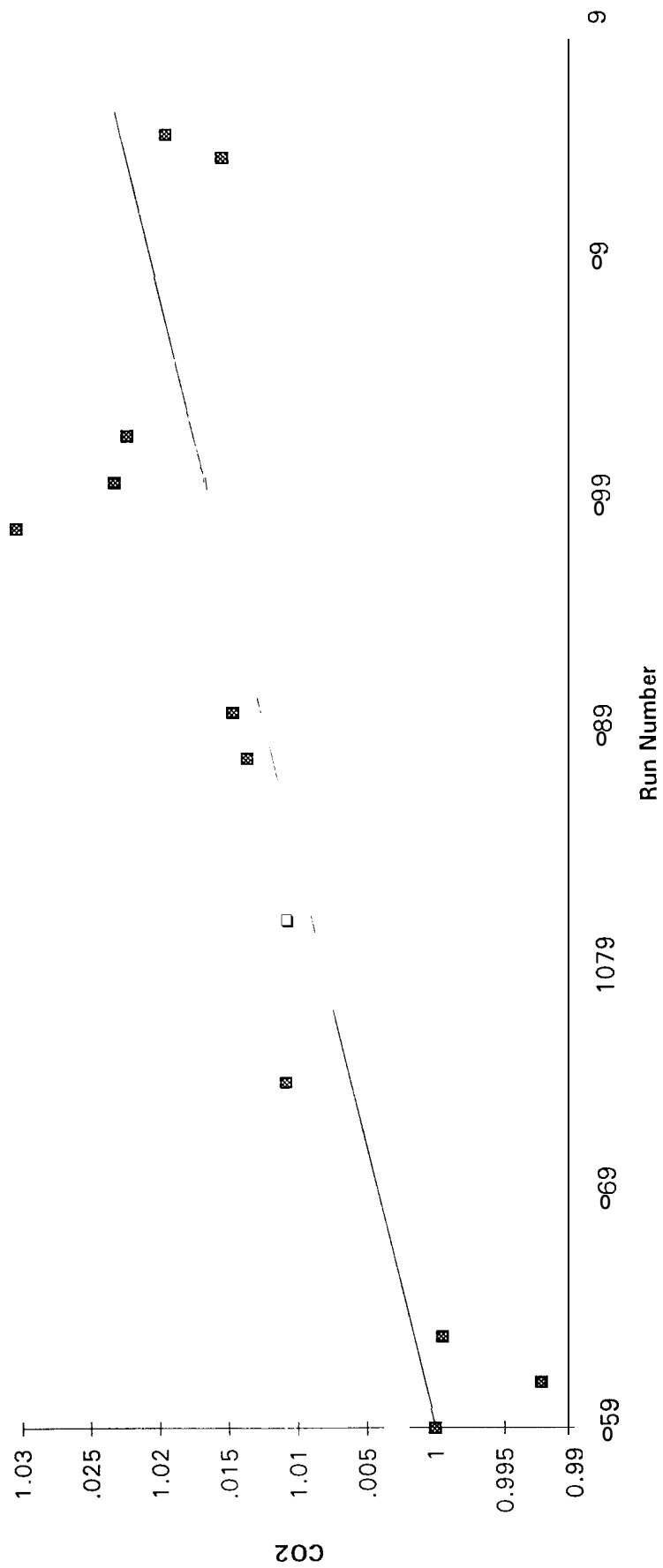


FIGURE 10 PM Correction Plot

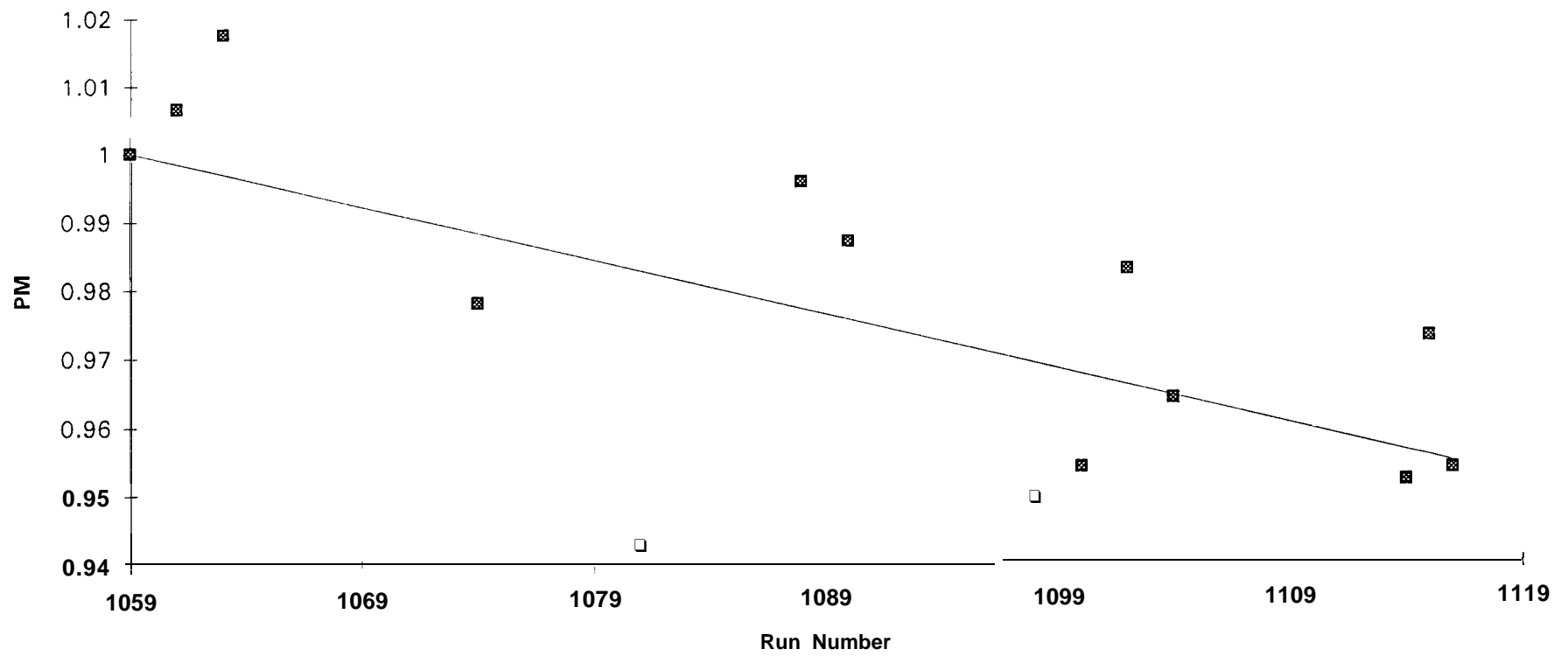


FIGURE 11 EFFECT OF BIODIESEL CONTENT ON HYDROCARBON EMISSION

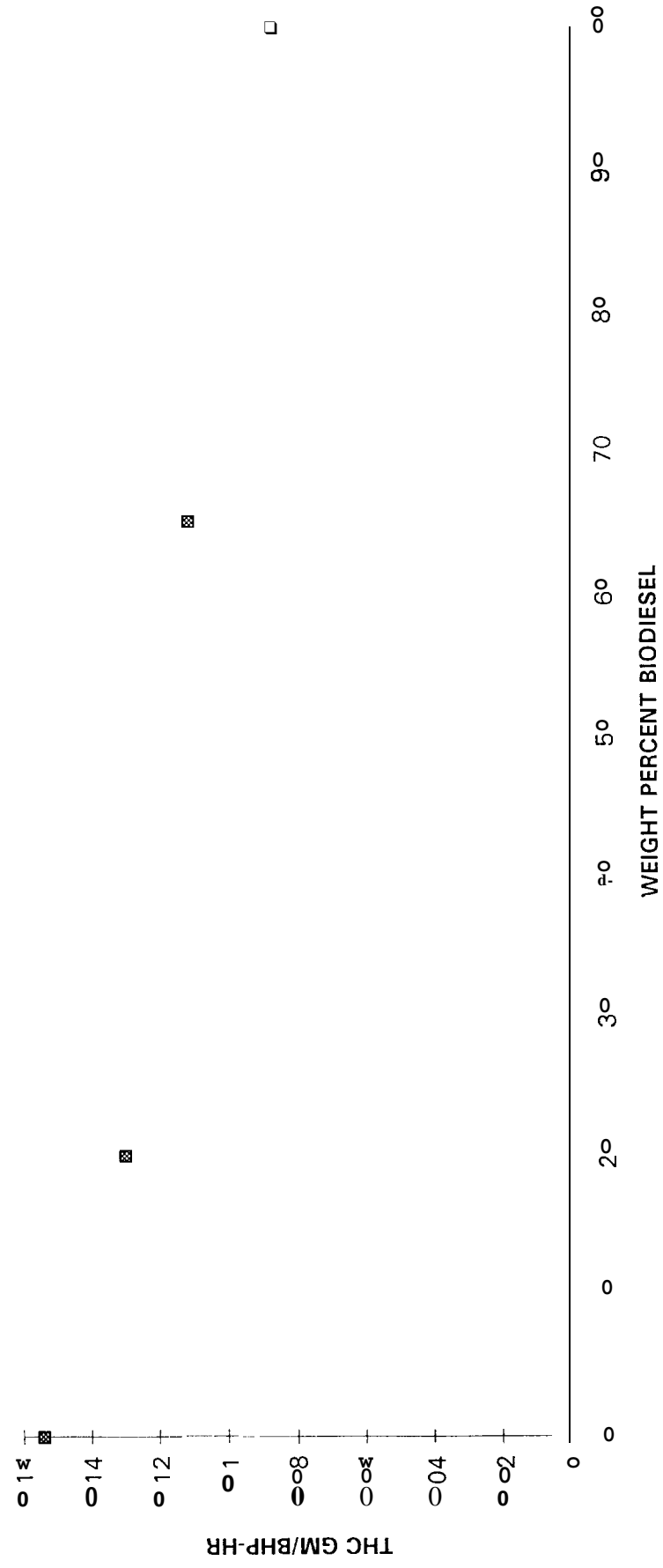


FIGURE 12 NOX EMISSION AS A FUNCTION OF BIODIESEL CONTENT

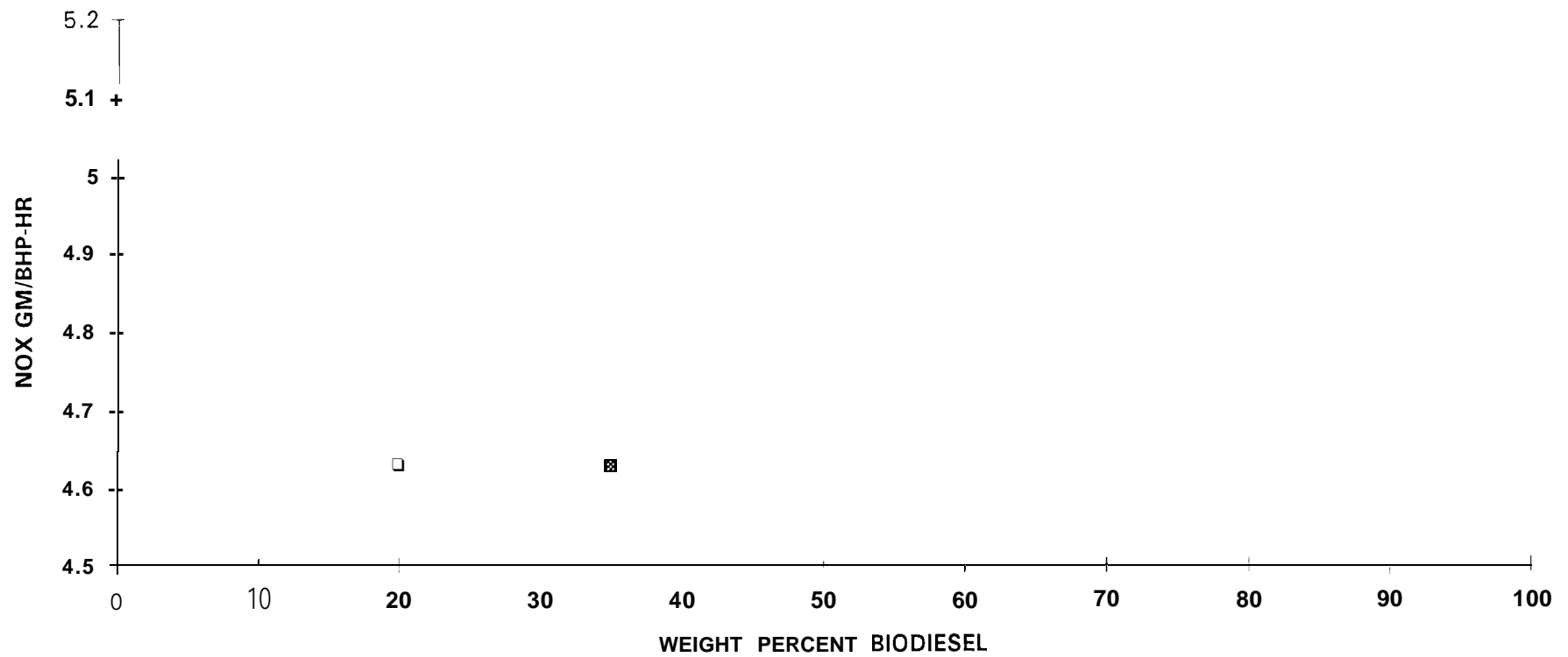


FIGURE 13 CO EMISSION AS A FUNCTION OF **BIODIESEL** CONTENT

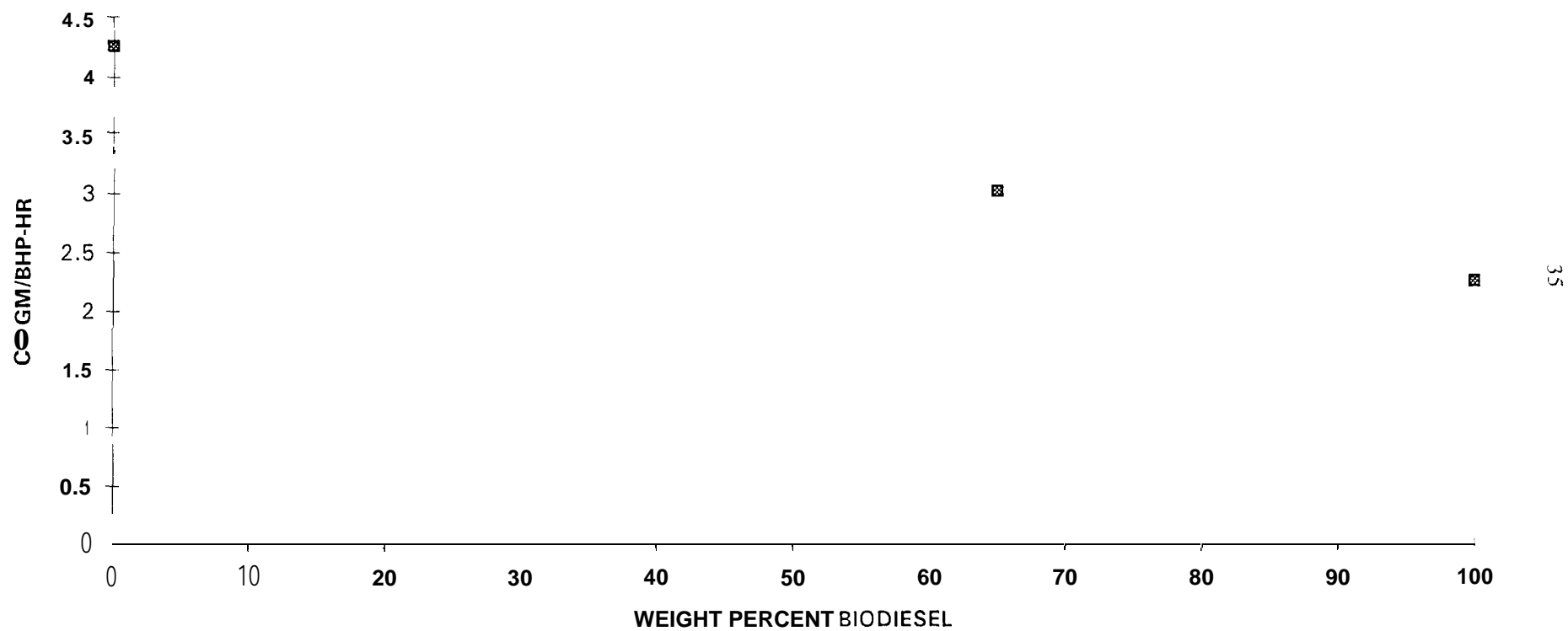


FIGURE 14 PM EMISSION AS A FUNCTION OF BIODIESEL CONTENT

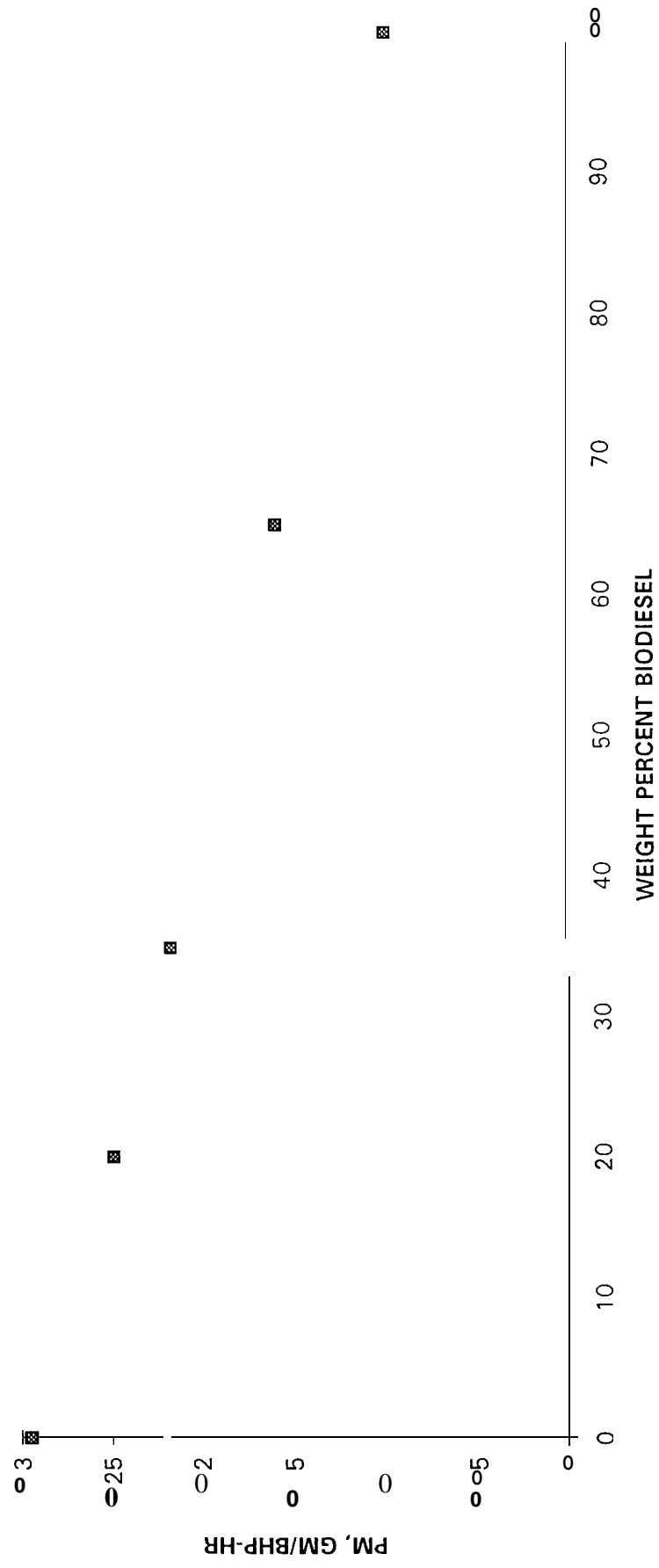


Figure 15

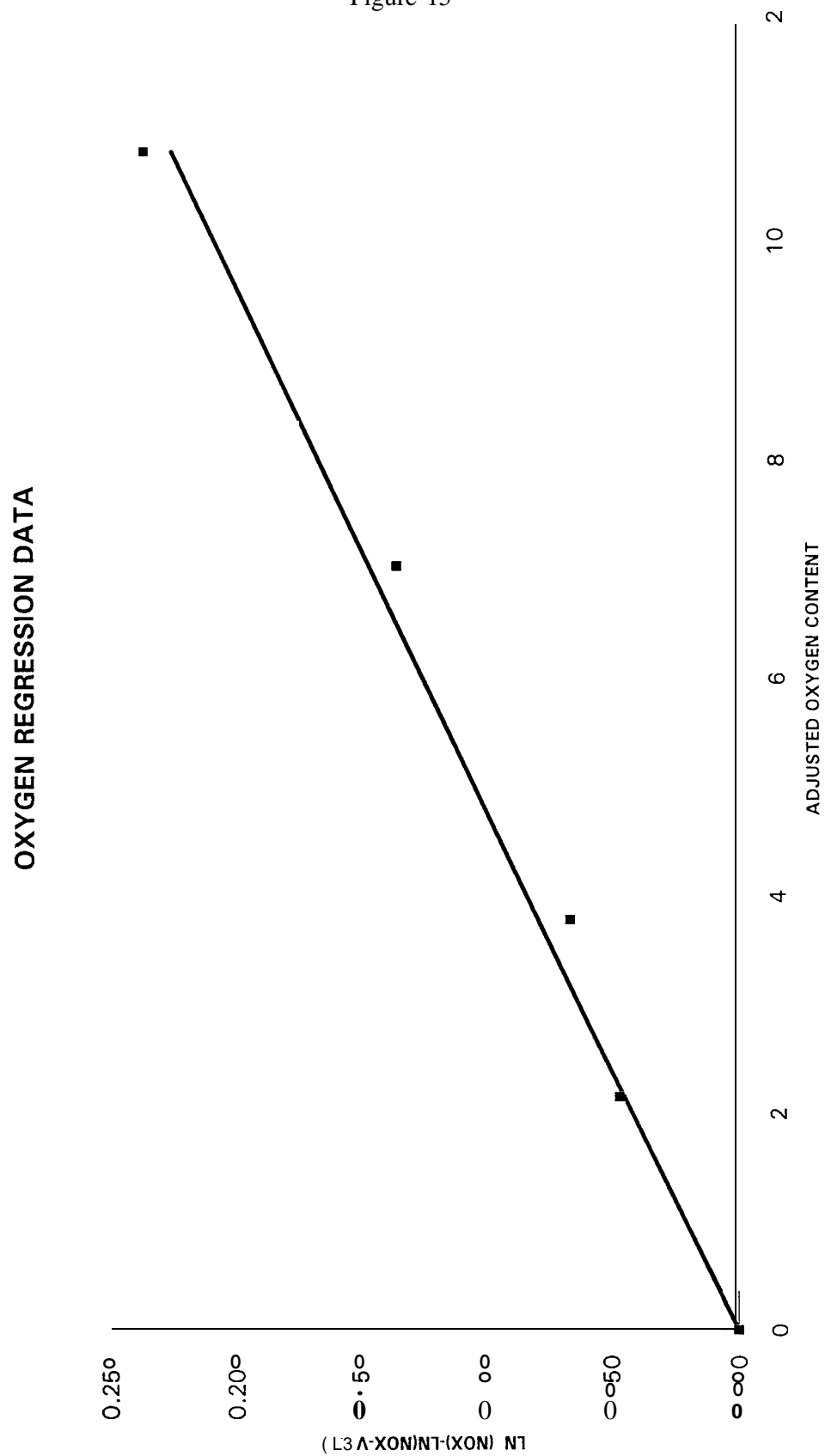


Figure 16

